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## PATENT ABSTRACTS OF JAPAN

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### (54) CONDUCTIVE COMPOSITION AND FLEXIBLE CONDUCTIVE MATERIAL

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a conductive composition having satisfactory flexibility, excellent stability when blending and storing, and satisfactory transparency, smoothness, and electric conductivity and provide a flexible conductive material preventing the reduction of electric conductivity due to a crack even if a soft basic material is expanded, shrunk, and deformed.

**SOLUTION:** The conductive composition containing water soluble conductive polymer having a sulfonic acid group and/or carboxyl group, vinyl polymer emulsion B having a glass-transition temperature of 40°C or less, and solvent and the flexible conductive material on which the conductive composition is applied are provided.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the conductor formed from the conductive constituent and this conductive constituent. It can apply to a flexible and porous base material good in more detail, and it has the high flexibility which holds conductivity, without the obtained conductor being destroyed by telescopic motion of a substrate base material, and it excels in the stability at the time of preservation at the time of combination, and is related with the flexibility conductor using the conductive constituent and it which can form good conductors, such as transparency, smooth nature, and conductivity.

[0002] The conductive constituent of this invention is applicable to the improvement in accumulation-of-electricity capacity of various antistatic agents, a capacitor, a cell, EMI shielding, a chemical sensor, a display device, a nonlinear ingredient, anticorrosives, adhesives, fiber, an antistatic coating, an anticorrosive paint, an electrodeposition paint, a plating primer, electric anticorrosion, and a cell etc. Since there are few conductive humidity dependencies and especially the conductor obtained from the conductive constituent of this invention has high flexibility, application to the antistatic agent of a flexible base material is excellent. As a concrete application as an antistatic agent, wrapping, a magnetic card, a magnetic tape, a magnetic disk, a photographic film, a printing ingredient, a conductive roll, a \*\* form film, a heat-sealing tape film, IC tray, IC carrier tape, a covering tape, etc. are mentioned.

[0003]

[Description of the Prior Art] Generally the approach of giving conductivity to plastics, using a conductive primer, an antistatic agent, etc. as a means for the static electricity clear trouble of plastics is used. The thing using conductive polymers, such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex salt and the poly aniline, metal system powder and carbon powder, and a surfactant as a conventional electric conduction component and the thing which combined these components and high molecular compounds are known. Moreover, the conductor which formed the electric conduction film on the base material as a conductor using the conductive paint which consists of said constituent is known. For example, in the conductive primer, in order to electric-conduction-ize a non-conductor front face, a conductive filler and a conductive conductive additive are added in a primer.

[0004] Although the conductive primer constituent for plastics (JP,58-76266,A, JP,61-218639,A, JP,2-120373,A, JP,2-194071,A) using conductive carbon, silver, nickel, aluminum, etc. as a conductive filler was proposed, since these conductive primer constituents for plastics were distributing the conductive filler, specifically, they had the fault which there is a possibility that a conductive filler and a resinous principle may dissociate and condense during storage, and is said that preservation stability is bad. Moreover, generally the conductive primer using these conductive fillers is an expensive rank, in order to acquire conductivity required further practically, it needs to thicken thickness, and it has a problem in respect of cost industrially.

[0005] Although the approach (JP,3-4970,A) using a surfactant cheap as an additive which gives conductivity is also proposed, conductivity changes with environments and it has the problem that conductivity falls remarkably under the environment where especially humidity is low. Moreover, many of conductive primers by which current use is carried out, and antistatic agents are organic solvent systems, and the alternative to a drainage system from problems, such as an environment and safety, is searched for.

[0006] In order to solve these technical problems, this invention persons devised the resin constituent for conductive covering (JP,11-185523,A). This constituent is a drainage system conductivity constituent which consists of a water-soluble conductive polymer, and a conductive constituent with good combination stability, conductivity, and transparency is obtained by using the specific Nonion system surfactant. However, since a crack occurs on the electric conduction film formed of telescopic motion of a base material, electric conduction pass is cut and conductivity may disappear when it applies to a porous and flexible base material like resin foam also in this constituent, it can apply to a flexible base material and the conductive constituent which can form a good adhesive and flexible conductor is called for.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the conductive constituent which does not produce the conductive fall by the crack even if it makes a base material expand and contract after flexibility is excellent in the stability at the time of preservation, forms good conductors, such as transparency, smooth nature, and conductivity, at fitness and the time of combination and forms a conductor in a base material with an especially flexible elastomer etc.

[0008]

[Means for Solving the Problem] That the trouble of these conventional techniques should be solved, as a result of examining a conductive constituent wholeheartedly, with the combination of the vinyl polymerization object of the water-soluble conductive polymer of specific structure, and specific physical properties, this invention persons find out that the conductive constituent suitable for a flexibility base material is obtained, and result in this invention.

[0009] That is, it is in the water-soluble conductive polymer (A) which has a sulfonic group and/or a carboxyl group, and the conductive constituent characterized by glass transition temperature containing a vinyl system polymer emulsion (B) 40 degrees C or less and a solvent (C) the first of this invention. Moreover, it is in the flexibility conductor which has the transparent conductive poly membrane formed when the water-soluble conductive polymer (A) which has the second sulfonic group of this invention and/or a carboxyl group, and glass transition temperature apply to a base material the conductive constituent containing the vinyl system polymer emulsion (B) and solvent (C) which are 40 degrees C or less.

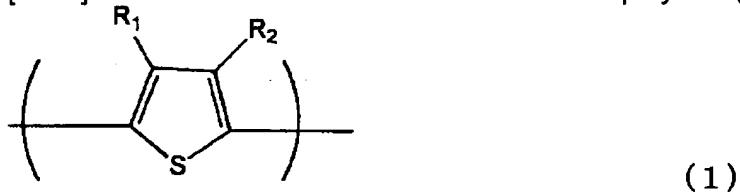
[0010]

[Embodiment of the Invention] Hereafter, the conductive constituent and flexibility conductor of this invention are explained to a detail. The water-soluble conductive polymer (A) used by this invention Although it will not be especially limited if it is the wafer-soluble conductive polymer which has a sulfonic acid and/or a carboxyl group, specifically JP,61-197633,A, JP,63-39916,A, JP,1-301714,A, JP,4-268331,A, JP,4-32848,A, JP,4-328181,A, JP,6-145386,A, JP,5-504153,A, JP,5-503953,A, JP,6-56987,A, JP,5-226238,A, JP,5-178989,A, JP,6-293828,A, JP,7-118524,A, The water-soluble conductive polymer shown in JP,6-32845,A, JP,6-87949,A, JP,6-256516,A, JP,7-41756,A, JP,7-48436,A, etc. is used preferably.

[0011] Still more specifically as a fusibility conductive polymer (A) No permuting and the permuted phenylenevinylene, vinylene, thienylene, On the frame of pi conjugated-system macromolecule which repeats at least one or more sorts chosen from the group which consists of PIRORIREN, phenylene, imino phenylene, iso thianaphthene, FURIREN, and cull BAZORIREN, and is included as a unit, or the nitrogen atom in this macromolecule The water-soluble conductive polymer which has the alkyl group or ether linkage \*\*\*\* alkyl group permuted by the sulfonic group and/or the carboxyl group or the sulfonic group, and/or the carboxyl group is mentioned. The water-soluble conductive

polymer which has the frame which contains thienylene, PIRORIREN, imino phenylene, phenylenevinylene, cull BAZORIREN, and iso thianaphthene also especially in this is used preferably.

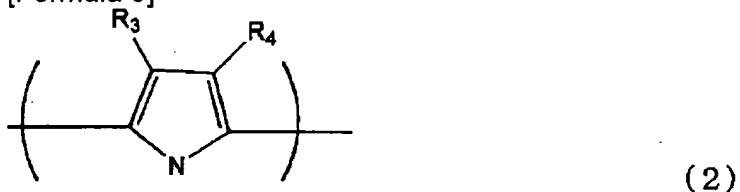
[0012] As a water-soluble desirable conductive polymer (A), it is [Formula 8].



the inside R1-R2 of the above-mentioned formula -- each -- independent -- H, -SO<sub>3</sub>-, and -SO<sub>3</sub>H -- - R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -F, -Cl, -Br, -I, -N (R35)2, -NHCOR35, -OH, It is chosen out of the group which consists of O-, -SR35, -OR35, -OCOR35, -NO<sub>2</sub>, -COO-, -R35COO-, -COOH, -R35COOH, -COOR35, -COR35, -CHO, and -CN. - Here R35 The alkyl, the aryl, the aralkyl radical, or alkylene of carbon numbers C1-C24, it is arylene or an aralkylene group, and is the radical chosen from the group which at least one of R1 and R2 becomes from -SO<sub>3</sub>-, -SO<sub>3</sub>H, -R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -COOH, -COO-, -R35COO-, and -R35COOH.

[0013]

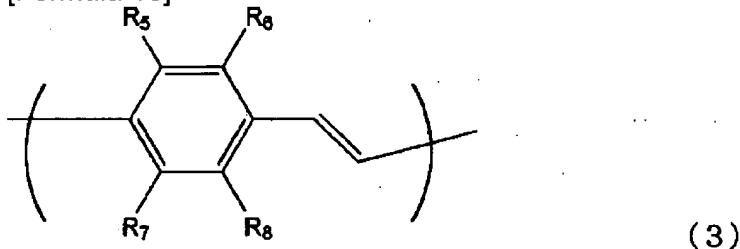
[Formula 9]



the inside R3 and R4 of the above-mentioned formula -- each -- independent -- H, -SO<sub>3</sub>-, and -SO<sub>3</sub>H -- - R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -F, -Cl, -Br, -I, -N (R35)2, -NHCOR35, -OH, It is chosen out of the group which consists of O-, -SR35, -OR35, -OCOR35, -NO<sub>2</sub>, -COO-, -R35COO-, -COOH, -R35COOH, -COOR35, -COR35, -CHO, and -CN. - Here R35 The alkyl, the aryl, the aralkyl radical, or alkylene of carbon numbers C1-C24, it is arylene or an aralkylene group, and is the radical chosen from the group which at least one of R3 and R4 becomes from -SO<sub>3</sub>-, -SO<sub>3</sub>H, -R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -COOH, -COO-, -R35COO-, and -R35COOH.

[0014]

[Formula 10]

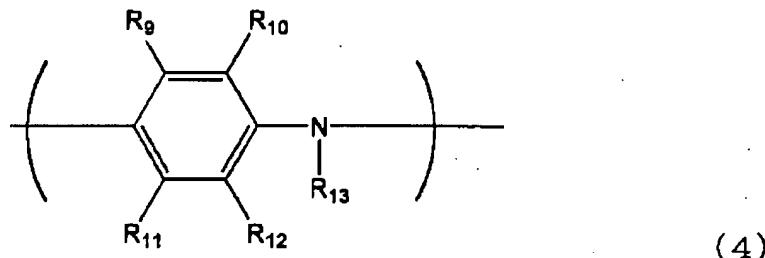


the inside R5-R8 of the above-mentioned formula -- each -- independent -- H, -SO<sub>3</sub>-, and -SO<sub>3</sub>H -- - R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -F, -Cl, -Br, -I, -N (R35)2, -NHCOR35, -OH, It is chosen out of the group which consists of O-, -SR35, -OR35, -OCOR35, -NO<sub>2</sub>, -COO-, -R35COO-, -COOH, -R35COOH, -COOR35, -COR35, -CHO, and -CN. - Here R35 The alkyl, the aryl, the aralkyl radical, or alkylene of carbon

numbers C1-C24, it is arylene or an aralkylene group, and is the radical chosen from the group which at least one of R5-R8 becomes from -SO<sub>3</sub>- , -SO<sub>3</sub>H, -R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -COOH, -COO-, -R35COO-, and -R35COOH.

[0015]

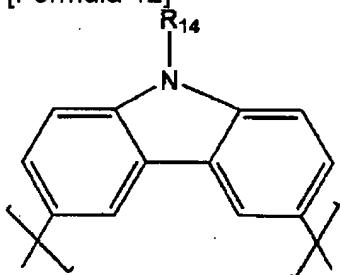
[Formula 11]



the inside R9-R13 of the above-mentioned formula -- each -- independent -- H, -SO<sub>3</sub>- , and -SO<sub>3</sub>H -- - R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -F, -Cl, -Br, -I, -N (R35)<sub>2</sub>, - NHCOR35, -OH, It is chosen out of the group which consists of O-, -SR35, -OR35, - OCOR35, -NO<sub>2</sub>, -COO-, -R35COO-, -COOH, -R35COOH, -COOR35, -COR35, -CHO, and -CN. - Here R35 The alkyl, the aryl, the aralkyl radical, or alkylene of carbon numbers C1-C24, it is arylene or an aralkylene group, and is the radical chosen from the group which at least one of R9-R13 becomes from -SO<sub>3</sub>- , -SO<sub>3</sub>H, -R35SO<sub>3</sub>- , -R35SO<sub>3</sub>H, -COOH, -COO-, -R35COO-, and -R35COOH.

[0016]

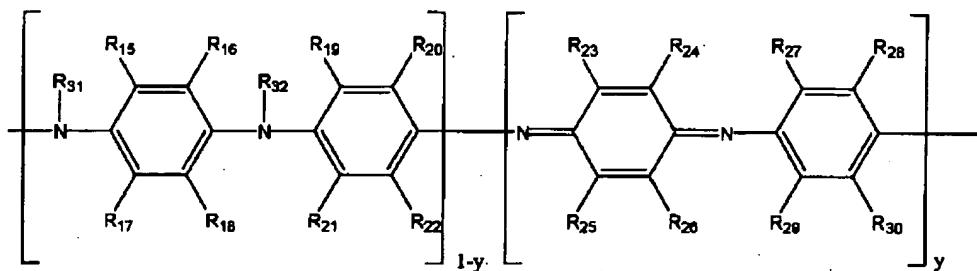
[Formula 12]



(5)

(It is chosen out of the group which consists of -SO<sub>3</sub>- , -SO<sub>3</sub>H, -R36SO<sub>3</sub>- , -R36SO<sub>3</sub>H, - COOH, -COO-, -R35COO-, and -R36COOH by the inside R14 of the above-mentioned formula. Here) R36 is the alkylene, the arylene, or the aralkylene group of carbon numbers C1-C24, from -- a conductive constituent given in any 1 term of claims 1-4 which include at least one repeat unit chosen from a group rather than it becomes 20 to 100% in the repeat unit of the whole polymer, and are characterized by molecular weight being 2000-1 million.

[0017] The following general formula (6) among the above-mentioned conductive polymers, [Formula 13]



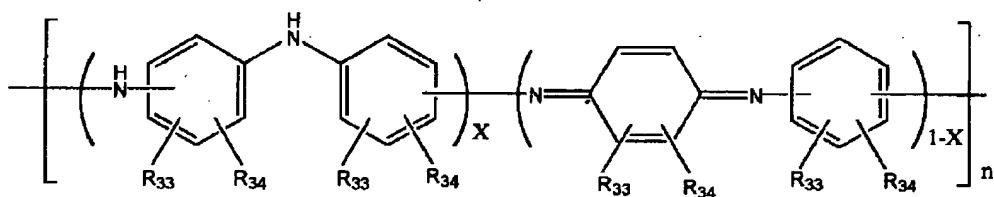
(6)

(y shows the number of the arbitration of  $0 < y < 1$  among the above-mentioned formula. Respectively R15-R32 independently) H, -SO<sub>3</sub>-, -SO<sub>3</sub>H, -R35SO<sub>3</sub>-, -R35SO<sub>3</sub>H, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -F, -Cl, -Br, -I, -N(R35) <sub>2</sub>, -NHCO<sub>3</sub>5, -OH, -O-, -SR35, -OCOR35, -NO<sub>2</sub>, -COO-, It is chosen out of the group which consists of R35COO-, -COOH, -R35COOH, -COOR35, -COR35, -CHO, and -CN. - Here R35 The alkyl, the aryl, the aralkyl radical, or alkylene of carbon numbers C1-C24, it is arylene or an aralkylene group, and is the radical chosen from the group which at least one of R15-R32 becomes from -SO<sub>3</sub>-, -SO<sub>3</sub>H, -R35SO<sub>3</sub>-, -R35SO<sub>3</sub>H, -COOH, -COO-, -R35COO-, and -R35COOH. The water-soluble conductive polymer which includes the repeat unit expressed 20 to 100% in the total of the repeat unit of the whole polymer is used more preferably.

[0018] Since 50% or more of water-soluble conductive polymer has very good solubility, the content of the sulfonic group to the total of a ring and a carboxyl group is used preferably here, and 100% of polymer is used especially preferably 90% or more still more preferably 70% or more more preferably.

[0019] Moreover, the substituent attached to a ring has a conductive and soluble field to a desirable electron releasing group, and its fusibility conductive polymer which an alkyl group, an alkoxy group, a halogen radical, etc. are desirable, and especially specifically has an alkoxy group is the most desirable.

[0020] They are the following general formula (7) and [Formula 14] also in such combination.



(7)

the inside R33 of the above-mentioned formula -- a sulfonic group, carboxyl groups, and those alkali-metal salts -- One radical chosen from the group which consists of ammonium salt and permutation ammonium salt is shown. R34 A methyl group, an ethyl group, n-propyl group, an iso-propyl group, n-butyl, iso-butyl, sec-butyl, tert-butyl, The dodecyl, a tetra-KOSHIRU radical, a methoxy group, an ethoxy radical, n-propoxy group, An iso-butoxy radical, a sec-butoxy radical, a tert-butoxy radical, one radical chosen from the group which consists of a heptoxy radical, a HEKUSO oxy-radical, an octoxy radical, a DODEKOKISHI radical, a tetra-KOSOKISHI radical, a fluoro radical, a chloro radical, and a BUROMO radical is shown, X shows the number of the arbitration of  $0 < X < 1$ , and n shows polymerization degree and is three or more. The water-soluble conductive polymer expressed is used most preferably.

[0021] That what is necessary is just to use a known approach as the manufacture approach of a water-soluble conductive polymer (A), although especially limitation is not carried out, the polymer which is made to carry out the polymerization of the polymerization nature monomers which have frames, such as thienylene, PIRORIREN, and imino phenylene, such as a heterocyclic compound and an aniline compound, with various synthesis methods, such as a chemistry oxidation style and an electrolytic oxidation method, and is obtained can be used, for example. For example, the synthetic approach of a publication is applied to JP,7-196791,A and JP,7-324132,A which this invention persons proposed.

[0022] As for the acidic group contained in the water-soluble conductive polymer used by this invention, it is desirable for the part to be a free-acid mold at least from the viewpoint of conductive improvement. Moreover, it is polyethylene-glycol conversion of GPC, 2000 or more things are excellent in conductivity, membrane formation nature, and film reinforcement, the mass mean molecular weight of the water-soluble conductive polymer used by this invention is used preferably, 3000 or more mass mean molecular weights and its 1 million or less thing are more desirable, and its 5000 or more and 500,000 or less thing is still more desirable. Here, although mass average molecular weight is excellent in solubility with 2000 or less polymer, conductivity and membrane formation nature may be insufficient, and although mass average molecular weight is excellent in conductivity in 1 million or more things, solubility is sometimes inadequate.

[0023] The vinyl system polymer emulsion (B) used by this invention Although it will not be limited especially if the glass transition temperature of a polymer is 40 degrees C or less For example, a methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, Methacrylic-acid i-butyl, t-butyl methacrylate, 2-ethylhexyl methacrylate, Alkyl methacrylate ester, such as methacrylic-acid n-lauryl, methacrylic-acid n-stearyl, and cyclohexyl methacrylate, A methyl acrylate, an ethyl acrylate, acrylic-acid n-butyl, acrylic-acid i-butyl, Acrylic-acid t-butyl, 2-ethylhexyl acrylate, acrylic-acid n-lauryl, Acrylic-acid alkyl ester, such as acrylic-acid n-stearyl and acrylic-acid cyclohexyl, Methacrylic-acid 2-hydroxyethyl, methacrylic-acid 4-hydroxy butyl, Methacrylic-acid hydroxyalkyl ester, such as methacrylic-acid 6-hydroxy hexyl, Acrylic-acid 2-hydroxyethyl, acrylic-acid 4-hydroxy butyl, Acrylic-acid hydroxyalkyl ester, such as acrylic-acid 6-hydroxy hexyl, Glycidyl group content vinyl polymerization nature monomers, such as glycidyl methacrylate and metaglycidyl acrylate, Aromatic series vinyl polymerization nature monomers, such as styrene and alpha methyl styrene, methacrylamide, Amide group content vinyl monomers, such as acrylamide and diacetone acrylamide, A methacrylic acid, an acrylic acid, an itaconic acid, a crotonic acid, a fumaric acid, a maleic acid, One or more sorts of monomers chosen from nitrile group content vinyl polymerization nature monomers, such as carboxyl group content vinyl polymerization nature monomers, such as a sorbic acid, and acrylonitrile, etc. (it is hereafter called a vinyl polymerization nature monomer (G).) A thing 40 degrees C or less is used for glass transition temperature with the included polymer or copolymer.

[0024] With the glass transition temperature in this invention, the value computed by guess types, such as an actual measurement or a formula of Fox, can be used. In this invention, the polymer glass transition temperature of a vinyl system polymer emulsion is 40 degrees C or less, and is 15 degrees C or less preferably. the flexibility of the conductor obtained here when glass transition temperature exceeds 40 degree C of \*\* -- \*\* -- since a conductor breaks by telescopic motion of a base material and electric conduction pass is cut when it falls remarkably and a conductor is formed in foam and a flexible and porosity base material like an elastomer, conductivity will disappear. Moreover, the minimum of the glass transition temperature of a polymer has desirable - 10 degrees C or more practically.

[0025] Although especially limitation is not carried out as the manufacture approach of a vinyl system polymer emulsion (B) used by this invention, when the approach of carrying out emulsification distribution of the vinyl system polymer compounded by solution polymerization etc. into a solvent, for example, the approach of carrying out the emulsion polymerization of the vinyl polymerization nature monomer (G), etc. are mentioned and the productivity of a conductive constituent is taken into consideration also in this, manufacturing by the emulsion-polymerization method is desirable. Furthermore, the approach of carrying out the emulsion polymerization of the vinyl polymerization nature monomer (G) in the solvent which dissolves or distributed the acidic group content vinyl polymerization object (F) acquired by the suspension-polymerization method as a describing [ above ] emulsion-polymerization method using the basic compound is more suitable.

[0026] Although especially limitation is not carried out as a solvent for the above-mentioned emulsion polymerizations, water or water, and a methanol, Alcohols, such as ethanol, isopropyl alcohol, propyl alcohol, and a butanol, Ketones, such as an acetone and an ethyl isobutyl ketone, ethylene glycol, Ethylene glycol, such as ethylene glycol methyl ether, propylene glycol, Propylene glycol methyl ether, propylene glycol ethyl ether, Propylene glycols, such as propylene glycol butyl ether and the propylene glycol propyl ether The mixed stock of pyrrolidones, such as amides, such as dimethylformamide and dimethylacetamide, or N-methyl pyrrolidone, and N-ethyl pyrrolidone, is used preferably. When using by mixed stock with water, water / organic solvent = 1 / 100 - 100/1 (mass ratio) are desirable.

(B)

Solvent

↑

[0027] An acidic group content vinyl system polymer (F) consists of acidic group content vinyl polymerization nature monomers, such as a methacrylic acid, an acrylic acid, a crotonic acid, and an itaconic acid, and a monomer containing one or more sorts chosen from the vinyl polymerization nature monomer (G). As for the solid content acid number of an acidic group content vinyl system polymer (F), it is desirable that it is 50-200 mgKOH/g, it is 70-150 mgKOH/g more preferably, and solubility, a water resisting property, and damp-proof balance become good especially in this range. When the solid content acid number uses a basic compound, may dissolve or be hard to distribute an acidic group content vinyl system polymer (I) in a solvent (C) in less than 50 mgKOH/g and exceeds 200 mgKOH/g, the water resisting property of a conductor, the moisture resistance, and base material adhesion which the distributed stability at the time of a suspension polymerization may fall, and are both acquired may fall.

[0028] Moreover, as for the mass average molecular weight of an acidic group content vinyl polymerization object (F), it is desirable that it is the range of 5000-50000, and it is the range of 8000-40000 more preferably. When mass average molecular weight is 5000 or less, the flexibility of a conductor in which the distributed stability at the time of a suspension polymerization may fall, and is acquired may fall and 50000 is exceeded, it may become difficult to use a basic compound, and to distribute or dissolve an acidic group content vinyl polymerization object (F) into a solvent.

[0029] the solution polymerization or emulsion polymerization at the time of manufacturing a vinyl system polymer emulsion (B) is well-known -- radical polymerization initiator use can be carried out and it can carry out on well-known polymerization conditions. A radical polymerization initiator specifically Azobisisobutyronitrile, Azo compounds, such as 2 and 2'-azobis (2,4-dimethylvaleronitrile), Inorganic peroxides, such as ammonium persulfate, potassium persulfate, and sodium persulfate, A benzoyl peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, Organic peroxide, such as cumene hydronium peroxide, potassium peroxide, peroxidation ammonium and a sodium hydrogensulfite, or the combination of a Rongalite, The redox system catalyst represented by the combination of organic

peroxide, such as t-butyl hydroperoxide and cumene hydronium peroxide, a sodium hydrogensulfate, or a Rongalite etc. is mentioned.

[0030] Although the addition of the above-mentioned radical polymerization initiator is the range of 0.01 - 10 mass %, when advance of a polymerization and control of a reaction are usually taken into consideration to the whole quantity of a vinyl polymerization nature monomer (G), its range of 0.1 - 5 mass % is desirable. Moreover, chelating agents which contain divalent iron ion, such as an iron sulfate, for activity grant of a polymerization initiator, such as a compound and disodium ethylenediaminetetraacetate, can be used.

[0031] Moreover, in the case of an emulsion polymerization, a well-known surfactant and a well-known chain transfer agent can be used if needed. As a surface active agent, the Nonion system surface active agents, such as anion system surface active agents, such as sodium dodecylbenzenesulfonate, lauryl sulfonic-acid sodium, and sodium lauryl sulfate, an anion system surface active agent containing a polyoxyethylene radical, the polyoxyethylene nonylphenyl ether, and the polyoxyethylene lauryl ether, the reactive surface active agent which has a vinyl polymerization nature double bond in a molecule are mentioned, for example. As a chain transfer agent, halogenated compounds, such as mercaptans, such as n-dodecyl mercaptan, n octyl mercaptan, n-tetradecyl mercaptan, and n-hexyl mercaptan, a carbon tetrachloride, and an ethylene bromide, can be mentioned, for example.

(F)  
surfactant

[0032] Especially an approach to teach the vinyl polymerization nature monomer (G) in an emulsion polymerization may not be limited, but may teach package preparation, dropping, or a part beforehand to a reaction container, and may use which approaches, such as the approach of trickling the remainder. When dropped, after being dropped at the surfactant water solution in a reaction container as it is, adding a surfactant to a dropping solution and carrying out preliminary emulsification, it may be dropped at a reaction container. Moreover, when using acid components, such as an acrylic acid, the preservation stability of an emulsion can also be raised by neutralizing after emulsion-polymerization termination.

[0033] A well-known initiator, a dispersant, and a chain transfer agent are used for an acidic group content vinyl polymerization object (F), and it is manufactured on well-known polymerization conditions. For example, as an example of an initiator, organic peroxide, such as azo compounds, such as azobisisobutyronitril, 2, and 2'-azobis (2,4-dimethylvaleronitrile), and a benzoyl peroxide, is mentioned. Moreover, as an example of a chain transfer agent, mercaptans, such as n-dodecyl mercaptan, n octyl mercaptan, n-tetradecyl mercaptan, and n-hexyl mercaptan, are mentioned.

[0034] As a basic compound for dissolving or distributing an acidic group content vinyl polymerization object (F) in a solvent, although especially limitation is not carried out, ammonia, triethylamine, tripropylamine, etc. are used preferably, for example. The amount of the basic compound used has the desirable range of 0.5-1Eq to the acidic group in the acidic group content vinyl system polymer (F) concerned. When in the case of less than 0.5Eq dissolve, or it is hard to distribute, the vinyl system polymer (F) concerned comes into a solvent and it exceeds 1Eq, the emulsion-polymerization stability of a vinyl polymerization nature monomer (G) may become poor.

(E)  
basic  
cpd

[0035] Moreover, as for the amount of the vinyl polymerization nature monomer (G) used to an acidic group content vinyl polymerization object (F), it is desirable that it is the range of the 50 - 300 mass section to the acidic group content vinyl system (polymer F) 100 mass section. The conductivity of the conductor obtained from the conductive constituent of this invention is easy to be spoiled by the case of under 50 mass sections. When exceeding the 300 mass sections, the emulsion-polymerization stability of a vinyl polymerization nature monomer (G) may become poor.

↑

[0036] As a solvent (C) used by this invention, water or water, and a methanol, Alcohols, such as ethanol, isopropyl alcohol, propyl alcohol, and a butanol, Ketones, such as an acetone and an ethyl isobutyl ketone, ethylene glycol, Ethylene glycol, such as ethylene glycol methyl ether, propylene glycol, Propylene glycol methyl ether, propylene glycol ethyl ether, Propylene glycols, such as propylene glycol butyl ether and the propylene glycol propyl ether The mixed stock of pyrrolidones, such as amides, such as dimethylformamide and dimethylacetamide, or N-methyl pyrrolidone, and N-ethyl pyrrolidone, is used preferably. When used by mixed stock with water, water / organic solvent =1 / 100 - 100/1 (mass ratio) are desirable.

[0037] Although surface active agents, such as an anion system surface active agent, the Nonion system surface active agent, and a cation system surface active agent, are used as a surface active agent (D) used for this invention, the surface active agent of the Nonion system is used preferably, and further, as for 16 or more Nonion system surface active agents, HLB raises the stability at the time of combination of a conductive constituent, and preservation, and it is more preferably used from making the appearance of the conductor obtained good. Moreover, as for the upper limit of HLB, from practical use, 30 or less are desirable. In addition, HLB is Hydrophile-Lipophile. It is the abbreviated name of Balance and is the index which shows the hydrophilic property of a surfactant etc.

[0038] An HLB value is mentioned for Above HLB and 16 or more polyoxyethylene alkylphenyl ETERU and an HLB value are mentioned for 16 or more polyoxyethylene alkyl ETERU as an example of 16 or more Nonion system surface active agents. 16 or more polyoxyethylene alkylphenyl ETERU has more little HLB especially, and especially since the stability at the time of combination and preservation and the amelioration effectiveness of the appearance of a conductor are acquired, it is desirable.

[0039] Although it will not be limited especially if the polyvinyl alcohol (E) used for this invention is usually polyvinyl alcohol of \*\*, especially, the denaturation polyvinyl alcohol which has an alkyl group at the end is used preferably, raises the stability at the time of combination of a conductive constituent, and makes the appearance of the conductor obtained good.

[0040] Especially if it is polyvinyl alcohol with which the alkyl group was introduced into the end as an example of denaturation polyvinyl alcohol of having an alkyl group at the end, it will not limit, but that 100-1000, and whose degree of \*\*-izing the repeat unit of 3-20, and a polyvinyl alcohol principal chain is 85 - 100% for the carbon number of an end alkyl group is more little, and especially since the stability at the time of combination and preservation and the amelioration effectiveness of a conductor appearance are acquired, it is desirable.

[0041] Even if it uses these surface active agents (D) and polyvinyl alcohol (E) for a conductive constituent independently, respectively, although effectiveness is acquired, it is using together and using and the improvement effectiveness in stability at the time of conductive, still bigger constituent combination is shown.

[0042] Next, the combination approach of the conductive constituent of this invention is explained concretely. Although especially limitation is not carried out, the combination approach of the conductive constituent of this invention For example, the approach of adding the powder or solution of a water-soluble conductive polymer (A), after adding a solvent (C) to a vinyl system polymer emulsion (B), Or the approach of adding the powder or solution of a good aquosity conductive polymer (A) etc. is mentioned to the vinyl system polymer emulsion (B) which made a surface active agent (D) and/or polyvinyl alcohol (E), and a solvent (C) contain beforehand.

[0043] Moreover, it may not be carried out, you may add as a surface active agent for emulsion polymerizations at the time of manufacture of a vinyl system polymer emulsion

(B), and especially limitation may also add the addition approach to the vinyl system polymer emulsion (B) of a surface active agent (D) at the time of termination of an emulsion polymerization.

[0044] Similarly, especially the addition approach to the vinyl system polymer emulsion (B) of polyvinyl alcohol (E) may not be limited, either, but you may add as a surfactant for emulsion polymerizations at the time of manufacture of a vinyl system polymer emulsion (B), and may add at the time of termination of an emulsion polymerization.

[0045] The range of the mass (a) of the water-soluble conductive polymer (A) used for this invention is 0.01-3 preferably [ that ratio / with the mass (b) of the vinyl system polymer in a vinyl system polymer emulsion (B) ] (a)/(b) adds so that it may become the range of 0.05-4 ], and more preferably. (a) When the conductivity of the conductor with which / (b) is obtained less than by 0.05 may become poor and 4 is exceeded, the deck watertight luminaire of the conductor with which the stability at the time of preservation can worsen, and moisture resistance may fall at the time of combination of a conductive constituent.

[0046] As for the mass (c) of the solvent (C) used for this invention, it is desirable that ratio [ with the mass (a) of a water-soluble conductive polymer (A) ] (a)/(c) adds so that it may become the range of 0.0001-5. (a) When the conductivity of the conductor with which the ratio of / (c) is obtained less than by 0.0001 may become poor and 5 is exceeded, the deck watertight luminaire of the conductor with which the stability at the time of preservation can worsen, and moisture-proof \*\* smooth nature may fall at the time of combination of a conductive constituent.

[0047] As for the mass (d) of the surface active agent (D) blended with the conductive constituent of this invention, it is desirable that ratio [ with the mass (b) of the vinyl system polymer in a vinyl system polymer emulsion (B) ] (d)/(b) adds so that it may become 0.001 - 0.1 range. (d) When / (b) is less than 0.001, the stability at the time of combination and preservation may worsen, and the appearance of the conductor obtained may also become poor. When exceeding 0.1, it may have a bad influence on the water resisting property and moisture resistance of a conductor.

[0048] Similarly, as for the mass (e) of the polyvinyl alcohol (E) blended with the conductive constituent of this invention, it is desirable that ratio [ with the mass (b) of the vinyl system polymer in a vinyl system polymer emulsion (B) ] (e)/(b) adds so that it may become 0.001 - 0.1 range. (e) When / (b) is less than 0.001, the stability at the time of combination and preservation worsens, and when the appearance of the conductor obtained may also become poor and it exceeds 0.1, it may have a bad influence on the water resisting property and moisture resistance of a conductor. Moreover, it is also desirable in the range of the above-mentioned addition to use together a surface active agent (D) and polyvinyl alcohol (E).

[0049] As a base material which carries out coating of the conductive constituent, a high molecular compound, wood, paper material, the ceramics and its film, foam, an elastomer, or a glass plate is used. for example, as a high molecular compound and a film, foam, and an elastomer Polyethylene, a polyvinyl chloride, polypropylene, polystyrene, polyester, ABS plastics, an AS resin, methacrylic resin, polybutadiene, a polycarbonate, Polyarylate, polyvinylidene fluoride, a polyamide, polyimide, Polyaramide, polyphenylene sulfide, a polyether ether ketone, There are polyphenylene ether, polyether nitril, polyamidoimide, a polyether ape phon, Pori Sall John, polyether imide, polybutylene terephthalate and its film, foam, an elastomer, etc.

[0050] It is desirable corona surface treatment or to carry out plasma treatment of the above-mentioned film front face in order for these high polymer films to make a transparent conductive poly membrane form in the one field at least, and to raise the adhesion of this high polymer film.

[0051] The conductive constituent used for forming the conductor of this invention is processed on the surface of a base material by the approach used for general coating. For example, dipping formers, such as the spraying approaches, such as the methods of application, such as a gravure coating machine, a roll coater, a curtain flow coater, a spin coater, a bar coating machine, a reverse coating machine, a kiss coating machine, a fan ten coating machine, a rod coating machine, an air doctor coating machine, a knife coating machine, a blade coating machine, a cast coating machine, and a screen coating machine, and spray coating, and a DIP, etc. are used. After processing it on the surface of a base material, you may dry at room temperature -250 degree C as occasion demands. As for the desiccation approach, ordinary temperature neglect, hot air drying, reduced pressure drying, etc. can choose the approach of arbitration.

[0052] Moreover, when applying to plastics base materials, such as polypropylene, for the improvement in base material adhesion of a conductor, it may mix with the emulsion of other resin, such as chlorinated polyolefins, or water soluble resin, and you may use. furthermore -- the conductive constituent of this invention -- the need -- responding -- a pigment, a defoaming agent, a film formation assistant, an ultraviolet ray absorbent, an anti-oxidant, a heat-resistant improver, and a leveling agent -- you may hang down and various additives, such as an inhibitor, a flattening, and antiseptics, may also be included.

[0053]

[Example] Hereafter, an example explains this invention in more detail. In addition, the "section" in an example shows the "mass section", and "mass %" is shown "%."

[0054] The example 1 of manufacture, a conductive polymer (A-1)

The stirring dissolution of the synthetic 2-aminoanisole-4-sulfonic-acid 100mmol of Pori (the 2-sulfo-5-methoxy -1, 4-imino phenylene) (A-1) was carried out at 25 degrees C at the aqueous ammonia solution of 4 mol/L, and the water solution of ammonium-peroxydisulfate 100mmol was dropped. After dropping termination and after stirring further at 25 degrees C for 12 hours, the resultant was dried after [ classified by \*\* ] washing, and 15g of polymer powder was obtained. The volume-resistivity values of this polymer were 9.0 ohm-cm.

[0055] The example 2 of manufacture, a conductive polymer (A-2)

Synthetic Pori (2-sulfo -1, 4-imino phenylene) in Pori (2-sulfo -1, 4-imino phenylene) (A-2) was compounded according to the known approach "J. Am.Chem.Soc., (1991), 113, 2665-2666." The sulfonic-acid content of the obtained polymer was 52% to the ring. The volume-resistivity values of this polymer were 50 ohm-cm.

[0056] The example 3 of manufacture, a conductive polymer (A-3)

Synthetic Pori (2-sulfo -1, 4-imino phenylene) in Pori (2-sulfopropyl -1, 4-imino phenylene) (A-3) was compounded according to the known approach "J.Chem.Soc., Chem.Commun., (1990), 180."

[0057] The example 4 of manufacture, a conductive polymer (A-4)

Synthetic Pori (2-sulfopropyl -2, 5-thienylene) in Pori (2-sulfopropyl -2, 5-thienylene) (A-4) was compounded according to the known approach (the collection of the 39th Society of Polymer Science, Japan drafts, and "1990, 561").

[0058] The example 5 of manufacture, a conductive polymer (A-5)

The stirring dissolution of the synthetic 2-aminoanisole-4-carboxylic-acid 100mmol of Pori (the 2-carbonyl -1, 4-imino phenylene) (A-5) was carried out at 25 degrees C at the aqueous ammonia solution of 4 mol/L, and the water solution of ammonium-peroxydisulfate 100mmol was dropped. After dropping termination and after stirring further at 25 degrees C for 12 hours, the resultant was dried after [ classified by \*\* ] washing, and 10g of polymer powder was obtained.

[0059] The example 6 of manufacture, a vinyl system polymer emulsion (B-1)

The deionized water 233 section, the ADEKA rear soap SE-10N(Asahi Denka Kogyo

make)3 section, and the emulgen 985(Kao Nonion system surface-active-agent, HLB=18.9) 6 section were taught to the flask equipped with an agitator, a capacitor, a temperature controller, a dropping pump, and nitrogen installation tubing, and stirring mixing was carried out. Furthermore, after carrying out a temperature up to 80 degrees C, teaching and stirring the 20 sections in the methyl-methacrylate (henceforth, MMA) 40 section, the acrylic-acid n-butyl (henceforth, BA) 28 section, and the mixture 100 section that consists of the KISHIRU (henceforth, EHA) 30 section and the methacrylic-acid (henceforth, MAA) 2 section to acrylic-acid 2-ethyl, the potassium persulfate (henceforth, KPS) 0.5 section was added under nitrogen-gas-atmosphere mind. After making it react for 30 minutes, the dropping polymerization of the remainder 80 section was carried out over 2 hours among the monomer mixture 100 previous sections. It held at 80 degrees C after dropping termination for 1 hour, and the vinyl system polymer emulsion (B-1) was obtained. The solid content of the obtained emulsion was 32%.

[0060] The example 7 of manufacture, a vinyl system polymer emulsion (B-2 and B-3) Except [ which indicated the monomer presentation and the surfactant to Table 1 ] having changed like, the polymerization was performed like the example 6 (B-1) of manufacture, and the vinyl system polymer emulsion (B-2 and B-3) was obtained.

[0061] The example 8 of manufacture, a vinyl system polymer emulsion (B-4)

The deionized water 200 section and the ADEKA rear soap SE-10N(Asahi Denka Kogyo make)3 section were taught to the flask equipped with the agitator, the capacitor, and the temperature controller, and were dissolved completely. After stopping stirring once, adding the MMA30 section, the EHA10 section, the BA44 section, the MAA16 section, the azobisisobutyronitril 0.5 section, and the n-dodecyl mercaptan 5 section, starting stirring again and carrying out a temperature up to 75 degrees C, as reaction temperature was maintained at 75-80 degrees C, it was made to react for 3 hours. The temperature up was carried out to 90 degrees C after that, and it maintained for 1 hour. The reactant was filtered with the sieve of 80 micrometers of openings, it dried and the vinyl system polymer (I) was obtained. The property of the vinyl system polymer (I) obtained in Table 2 is shown.

[0062] The vinyl system (polymer I) 100 section and the deionized water 410 section were taught to the flask equipped with an agitator, a capacitor, a temperature controller, a dropping pump, and nitrogen installation tubing. Stirring, the aqueous ammonia 10 section was added 28%, 80 more degree-C temperature up of the stirring was continued and carried out for 30 minutes, it stirred for 1 hour, and the aquosity liquid of a vinyl system polymer (I) was obtained. After adding the KPS0.5 section under nitrogen-gas-atmosphere mind, keeping temperature at 80 degrees C, the dropping polymerization of the pre emulsion which stirred and prepared the mixture of the MMA20 section, the BA60 section, the glycidyl methacrylate (henceforth, GMA) 10 section, the ADEKA rear soap SE-10N(Asahi Denka Kogyo make)5 section, and the deionized water 50 section was beforehand carried out over 1 hour. It held at 80 degrees C after dropping termination for further 1 hour, and the vinyl system polymer emulsion (B-3) was obtained. The solid content of the obtained emulsion was 31%.

[0063] The example 9 of manufacture, a vinyl system polymer emulsion (B-5 and B-6) Except [ which indicated the monomer presentation to Table 2 ] having changed like, the polymerization was performed like the example 8 (B-4) of manufacture, and the vinyl system polymer emulsion (B-5 and B-6) was obtained.

[0064] Stirring the example 1 - 5 vinyl system polymer emulsion 30 section, the 10% water-solution 10 of a water-soluble conductive polymer section was added, and the conductive constituent was obtained (solid content \*\*10/90 of the solid content / vinyl system polymer of a conductive polymer). The property of the obtained conductive constituent is shown in Table 3.

[0065] The emulgen 985 (the Kao Nonion system surfactant, HLB=18.9) of the amount shown in Table 3 at the example 6 - 10 vinyl system polymer emulsion 30 section (solid content \*\*9 section of a vinyl system polymer) and/or denaturation PVA MP-103 (denaturation PVA by Kuraray Co., Ltd.) were added, and it stirred for 1 hour. Stirring furthermore, the 10% water-solution 10 of a conductive polymer (A-1) section (solid content of a conductive polymer = one section) was added, and the conductive constituent was obtained. The property of the obtained conductive constituent is shown in Table 3.

[0066] Stirring the example 1 of a comparison, and the 3 vinyl system polymer emulsion 30 section, the 10% water-solution 10 of a conductive polymer (A-1) section was added, and the conductive constituent was obtained (solid content \*\*10/90 of the solid content / vinyl system polymer of a conductive polymer). The property of the obtained conductive constituent is shown in Table 3.

[0067] The emulgen 985 (the Kao Nonion system surfactant, HLB=18.9) of the amount shown in Table 3 at the example 2 of a comparison and the 4 vinyl system polymer emulsion 30 section (solid content \*\*9 section of a vinyl system polymer) and/or denaturation PVA MP-103 (denaturation PVA by Kuraray Co., Ltd.) were added, and it stirred for 1 hour. Stirring furthermore, the 10% water-solution 10 of a conductive polymer (A-2) section (solid content of a conductive polymer = one section) was added, and the conductive constituent was obtained. The property of the obtained conductive constituent is shown in Table 3.

[0068] Evaluation of the engine performance in an example and the example of a comparison was performed using the approach shown below.

(1) Combination stability : visual evaluation of the stability immediately after combination of a conductive constituent was carried out.

O Aggregate-less \*\* aggregate generation x under conductive polymer water-solution addition -- coagulation (2) conductor appearance: -- the blended conductive constituent was applied with the bar coat on the glass plate, it heated at 100 degrees C after 1-hour desiccation with the room temperature for 1 hour, and the trial conductor of 10 micrometers of thickness was produced. Visual evaluation of the appearance of a trial conductor was carried out.

O It is smooth and is transparency fitness x. A front face is uneven and it is opacity [0069]. (3) conductive: -- the surface electrical resistance of a conductive covering surface -- Huy Lester -- it measured depending on the method of 2 terminals using "Mitsubishi Chemical MCP-TESTER."

(4) Flexibility : sinking-in spreading of the blended conductive constituent was carried out at polyethylene foam, it heated at 80 degrees C for 2 hours, and the test piece was created. It contracted to the test piece by 1kg of loads, and the conductivity after stopping a load and repeating telescopic motion of \*\*\*\*\* 100 times was measured.

O Change[ conductive ]-less x Conductive disappearance [0070]

[Table 1]

	ビニル系重合体エマルション		
	B-1	B-2	B-3
MMA	40	43	70
BA	28	25	28
EHA	30	30	-
MAA	2	2	2
ガラス転移温度	8.4	13	61
固形分(%)	32	32	32

ホモポリマーのガラス転移温度：

MMA : 105°C.

BA : -54°C.

EHA : -70°C.

MAA : 130°C

[0071]

[Table 2]

		ビニル系重合体エマルション		
		B-4	B-5	B-6
ビニル系重合体(I)	MMA	30	34	64
	BMA	10	36	10
	BA	44	14	10
	MAA	16	15	16
ビニル重合性単量体(II)	MMA	20	30	50
	BA	60	60	40
	GMA	10	10	10
ビニル系重合体(I)の酸価(mgKOH/g)	104	104	104	
ビニル系重合体(I)の重量平均分子量	10000	10000	9000	
ビニル系重合体Tg	8.8	14.5	61	
エマルション固形分(%)	31	30	30	

ホモポリマーのガラス転移温度： GMA : 74°C

酸価：ビニル重合体1 g に含まれる酸性基を中和するのに必要な水酸化カリウムのmg数

重量平均分子量：GPCを用いて測定した標準ポリスチレン換算の重量平均分子量

[0072]

[Table 3]

	可溶性導電性 ポリマー	ビニル 重合体 エマルション	界面活性剤 *)	ポリビニル アルコール#2	配合安定性	導電体外観	表面抵抗 (Ω)	柔軟性 評価
実施例1	A-1	B-1	—	—	○	○	$1 \times 10^7$	○
2	A-2	B-1	—	—	○	○	$7 \times 10^7$	○
3	A-3	B-1	—	—	○	○	$1 \times 10^4$	○
4	A-4	B-1	—	—	○	○	$9 \times 10^7$	○
5	A-5	B-1	—	—	○	○	$2 \times 10^8$	○
6	A-1	B-2	0.3	—	○	○	$3 \times 10^7$	○
7	A-1	B-4	0.3	—	○	○	$2 \times 10^7$	○
8	A-1	B-4	0.3	0.3	○	○	$4 \times 10^7$	○
9	A-1	B-5	0.3	—	○	○	$3 \times 10^7$	○
10	A-1	B-5	0.3	0.1	○	○	$5 \times 10^7$	○
比較例1	A-1	B-3	—	—	×	×	測定不可	測定不可
2	A-2	B-3	0.8	—	○	○	$5 \times 10^8$	×
3	A-1	B-6	—	—	×	×	測定不可	測定不可
4	A-2	B-6	0.3	0.1	○	○	$6 \times 10^4$	×

\*1界面活性剤：花王社製ノニオン系界面活性剤（商品名エマルゲン985=HLB18.9）

\*2ポリビニルアルコール：クラレ社製変性ポリビニルアルコール（商品名MP-103）

界面活性剤、ポリビニルアルコール添加量はビニル重合体エマルジョン固形分9部に対する

比率（部）

### [0073]

[Effect of the Invention] At the time of combination, the flexibility conductor which does not produce the conductive fall by the crack even if it makes a base material expand, contract and transform after excelling in the stability at the time of preservation, being able to form good flexibility conductors, such as transparency, smooth nature, and conductivity, and forming a conductor in a flexible base material is obtained, and the conductive constituent of this invention is very useful on industry.

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[Translation done.]